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November 15, 2005

The Journal of Chemical Physics

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First principles study of the aggregation of oligo and polythiophene cations in solution

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(Dated: November 8, 2005)

Abstract

The stacking of positively charged (or doped) terthiophene oligomers and quaterthiophene polymers in solution is investigated applying a recently developed unified electrostatic and cavitation model for first-principles calculations in a continuum solvent. The thermodynamic and structural patterns of the dimerization are explored in different solvents, and the distinctive roles of polarity and surface tension are characterized and analyzed. Interestingly, we discover a saturation in the stabilization effect of the dielectric screening that takes place at rather small values of ϵ_0 . Moreover, we address the interactions in trimers of terthiophene cations, with the aim of generalizing the results obtained for the dimers to the case of higher order stacks and nanoaggregates.

I. INTRODUCTION

The intermolecular interactions between conjugated polymers and oligomers in the condensed phase—whether in the solid state or in solution—entail a fundamental interest in the emerging field of molecular electronics, as they are decisive factors in the electronic and structural properties of the material. The orientation and alignment of polymers in a solid matrix, the formation of aggregates in films and solution, or the ability of organic semiconductors to self-assemble, are the outcome of a complex balance between the spatial features of the molecules and the substrate, and the interactions between them at the synthesis conditions.^{1–6} By dictating the rules for aggregation, these interactions eventually shape properties such as charge delocalization and mobility^{2,6–8} or optical^{3,9–11} and electromechanical¹² response.

Thiophene derived oligomers and polymers represent today one of the most promising class of organic semiconductors, finding potential applications in a variety of electronic and electroactive devices.^{13–15} Semiconducting properties arise with doping, therefore much of the basic research performed on these systems has addressed in particular the doped or oxidized species. Since the early nineties electrochemical and spectroscopic evidence was gathered indicating that oxidized oligothiophenes reversibly associate in solution.^{16–18} In a recent study,¹⁹ we have claimed that this association can be dissected in three contributions: the attractive π - π interactions, the Coulombic repulsion, and the effect of the solvent. In the case of oligothiophene cations dimers, combination of semioccupied HOMOs form occupied bonding and empty antibonding orbitals, resulting in an interaction of covalent character, different in nature to the one arising in neutral dimers, of dispersive origin.²⁰ In vacuum, the electrostatic repulsion between the cations largely exceeds the covalent term,^{19,21} making

manifest the importance of the solvent (or of the counterions in the solid state case) in stabilizing the stacks. A polarizable dielectric medium favors the concentration of charge in a small cavity, reverting the balance from net repulsion to attraction and stacking.

In the present paper, we employ a first principles approach recently developed to describe the effect of a continuum solvent within the Car-Parrinello, density-functional theory framework,²² and use it to explore the role of polarity and surface tension in the stabilization of dimers of polythiophene and oligothiophene radical cations. Furthermore, we examine the possibility of trimer formation, as an intermediate step toward the genesis of higher order aggregates, and to gain insight on the self-assembly phenomenon from a solution. In charged dimers, unlike the case of neutral dimers governed by van der Waals forces, interactions are predominantly covalent and electrostatic, and density-functional theory (DFT) has proven to perform consistently with highly-correlated quantum-chemistry methods.¹⁹ In our approach, the contribution of the surface tension to the solvation free energy is computed in a very natural fashion, as the product between the area of the cavity and the surface tension of the solvent.²² This contribution is particularly important in a dimerization process, where the fusion of two cavities into one provides an additional stabilizing term associated to the minimization of the total cavity area.

II. METHODOLOGY

All calculations in this work have been performed with the public domain Car-Parrinello parallel code included in the Quantum-ESPRESSO package,²³ based on density-functional theory (DFT), periodic-boundary conditions, and plane-wave basis sets. Vanderbilt ultrasoft pseudopotentials²⁴ have been used to represent the ion-electron interactions, in combination with the PBE approach to the exchange-correlation term,²⁵ and with the Kohn-Sham orbitals

and charge density expanded in plane waves up to a kinetic energy cutoff of 25 and 200 Ry respectively.

We employ a continuum solvent model recently implemented in the Quantum-ESPRESSO package and described in detail in reference ²². In this scheme, the solvent is represented as a dielectric medium surrounding a quantum-mechanical solute confined in a cavity delimited by an isosurface of the electron density. In this context the solvation free energy ΔG_{sol} can be regarded as the sum of several components, usually:

$$\Delta G_{sol} = \Delta G_{el} + \Delta G_{cav} + \Delta G_{dis-rep} \quad (1)$$

where ΔG_{el} , ΔG_{cav} , and $\Delta G_{dis-rep}$ are the electrostatic, the cavitation, and the dispersion-repulsion contributions respectively.²⁶ In our implementation ΔG_{el} and ΔG_{cav} are considered explicitly, while $\Delta G_{dis-rep}$ is largely seized by virtue of the parametrization, as part of the electrostatic term. In the next two paragraphs the approaches to obtain ΔG_{el} and ΔG_{cav} are briefly reviewed.

The electrostatic interaction between the dielectric and the solute is calculated as proposed by Fattbert and Gygi,^{27,28} solving the Poisson equation in the presence of a dielectric continuum with a permittivity $\epsilon[\rho]$,

$$\nabla \cdot (\epsilon[\rho] \nabla \phi) = -4\pi \rho . \quad (2)$$

The function $\epsilon[\rho]$ is defined to asymptotically approach the permittivity of the bulk solvent ϵ_0 in regions of space where the electron density is low, and 1 in those regions where it is high.²² In this way the dielectric medium and the electronic density respond self-consistently to each other through the dependence of ϵ on ρ and vice-versa. The variation in the dielectric constant at the solvent-solute interface is controlled by the two parameters ρ_0 and β , which determine the size of the cavity and the smoothness of the transition respectively. These are

virtually the only parameters entering the model. The adopted values, $\rho_0=0.00078$ e and $\beta=1.3$, represent a rather universal choice.²²

The cavitation term is computed as the product between the surface tension of the solvent γ and the area of the cavity,

$$\Delta G_{cav} = \gamma S(\rho_0), \quad (3)$$

where $S(\rho_0)$ is the surface of the same cavity employed in the electrostatic part of the solvation energy and is defined by an isosurface of the charge density. This area can be easily and accurately calculated by integration in a real-space grid, as the volume of a thin film delimited between two charge density isosurfaces, divided by the thickness of this film. This idea has been originally proposed by Cococcioni et al.²⁹ to define a “quantum surface” in the context of extended electronic-enthalpy functionals.

III. RESULTS AND DISCUSSION

Crystallographic data³⁰ and recent calculations^{19,21} on oxidized dimers have indicated that the stacking of oligothiophene cations follows a “slipped” pattern where the layers are shifted along the molecular axis, as shown in Fig. 1. We have studied the dependence of the energy as a function of the lateral shift for oxidized terthiophene and polyquaterthiophene dimers in acetonitrile, with $\epsilon_0=35.7$ and $\gamma=28.7$ mN/m, at a fixed intradimer separation of 3.4 Å. The total charge of these systems is +2 (in the polymer, there is a positive charge every four thiophene rings). The results are showed in Fig. 2: both the oligomer and the polymer exhibit a similar pattern, with a global minimum at 2.3 Å for the terthiophene and 2.0 Å for the polythiophene. A local minimum at 0.0 Å (where the two layers are overlapping) is present in both cases. Interestingly, the net binding is very sensitive to the

lateral shift, varying steeply in a range of 10 kcal/mol as one layer is slipped along the other. At shifts of about 1 Å off the minima, the π - π interaction between the cations appears clearly weakened, resulting in an unbound dimer.

The nature of the solvent doesn't have any significant effect on this characteristic pattern, even if it affects the magnitude of the interaction. This is shown in Fig. 3, where the terthiophene curve is displayed in three different media: acetonitrile, dichloromethane ($\epsilon_0=8.9$, $\gamma=27.2$ mN/m) and water ($\epsilon_0=78.8$, $\gamma=72.2$ mN/m). Fig. 4 explicitly illustrates the role of the solvent in the binding of the terthiophene cations, by showing the interaction energy as a function of the intradimer distance at a fixed lateral shift of 2.3 Å. The binding energies are close to 5 kcal/mol for dichloromethane and acetonitrile, and 12 kcal/mol in water. These values can be seen as a lower limit for the dimerization enthalpy ΔH_d , since the effect of the ionic environment was neglected in the calculations (the counterions in solution would differentially stabilize the doubly-charged terthiophene dimer compared to two terthiophene cations. This effect has been recently discussed by Jakowski and Simons³¹ for dimers of tetracyanoethylene anions, $[\text{TCNE}]_2^{2-}$). In fact, dimerization enthalpies between 7 and 14 kcal/mol have been reported for different terthiophene derivatives in apolar solvents.^{32–34} The interplanar separations corresponding to the minima, in the range of 3.4 to 3.5 Å, are consistent with the distance of 3.47 Å obtained for substituted terthiophene cations in the solid state.³⁰ Fig. 5 compares the potential energy surface of the oligomer with the one corresponding to the polymer (the later was calculated at a fixed lateral shift of 2.0 Å). The equilibrium distance turns out around 0.3 Å larger in the periodic system, although it exhibits a slightly stronger binding. This is in agreement with experimental data showing that ΔH_d is enhanced by the length of the chain,¹⁷ a trend related to a “dilution” of the Coulombic repulsion as the ratio between charge and oligomer size decreases.¹⁹ At

the same time, however, the increase in length at a given oxidation state would diminish the ratio between unpaired electrons available to π - π bonding and thiophene rings, what would presumably revert the aforementioned binding trend starting from certain molecular weight.³⁵

The separate roles played by the dielectric screening of the solvent and its surface tension in the stabilization of the dimer are highlighted in Fig. 6. If the contribution of ΔG_{cav} were omitted, the binding curves would turn out to be very close to each other (Fig. 6a). The larger γ in the case of water (72.2 mN/m versus 28.7 mN/m in acetonitrile) is responsible for the deeper minimum in the potential energy surface. The net effect of the surface tension is to minimize the area of the solvation cage, monitored in Fig. 6b as the cations are pulled apart. Beyond certain separation—of about 4.75 Å—the surface remains constant, indicating that the single cavity has split and each cation is enclosed in a separate cavity of area independent of the interplanar distance. In this situation there is no cavitation energy gain and therefore the curves excluding and including ΔG_{cav} (open and closed symbols in Fig. 6a respectively) overlap on the right part of the plot.

The potential energy curves in Fig. 6a unveil an intriguing possibility: that the binding energy is not directly related to the dielectric constant of the solvent, as our intuition may suggest. This hypothesis is explored in Fig. 7, where the interaction energy between two terthiophene cations separated by 3.6 Å is plotted as a function of the dielectric constant, ignoring the contribution of the surface tension. The results are somehow unexpected: a rather small increase in the permittivity coming from the vacuum rapidly stabilizes the dimer, but once the dielectric constant is above 10 the effect of a further increase in polarity is minor. This behavior can be rationalized considering that a polarizable dielectric medium with low permittivity is already enough to screen most of the Coulombic repulsion between

the two charges and to favor the grouping of these charges by polarizing itself. The positive drift that is observed at higher permittivities for $\rho_0=0.00078\ e$ is an artifact of the continuum model. Since the dielectric constant is defined as a continuous function of the electron density, its value throughout the intradimer region may depart from 1, allowing the dielectric medium to fill some of the space between the cations and to interfere, though modestly, with the π - π bond. This effect will be enhanced at large values of ϵ_0 and ρ_0 . In reality, instead, the solvent would not penetrate the intradimer space if the separation is $3.6\ \text{\AA}$, regardless of ϵ_0 . This spurious behavior is in fact absent in the curve computed with $\rho_0=0.0003$ in Fig. 7. What is remarkably captured by the continuum model is a saturation of the effect of polarity on the dimerization occurring already at a very low dielectric constant. These results are pretty much consistent with experimental observations that turn down a direct correlation between the dimerization trend and the polarity of the medium, while emphasizing the dependence on the solubility of the oligothiophenes.³⁶ To understand the effect of the solvent on ΔH_d , then, one should consider other properties such as surface tension or specific interactions between the solute and the medium.

Are the thermodynamic and structural features found so far for the dimerization, applicable to the stacking of multiple oligomer layers? It would be very interesting to know if or how the present results can be extended to processes such as nanoaggregation and self-assembly in solution, involving the collective pairing of many oligothiophene units. In an attempt to offer an answer, even if preliminary, to this question, we have studied the formation of trimers of terthiophene cations in acetonitrile. Fig. 8 depicts the two configurations of minimum energy obtained for the trimer in acetonitrile, in which the third cation is shifted $+ \text{ or } - 2.3\ \text{\AA}$ with respect to the next oligomer. As shown in Fig. 9, there is no significant energetic difference between these two minima. The curve corresponding to the

dimer is plotted in the same figure: the pattern of valleys and peaks is preserved at the same lateral displacements when increasing the number of layers from two to three. The differences in the relative depths of these curves can be ascribed to the fact that the same interplanar separation of 3.4 Å was adopted in the calculation of both, but the optimal separation in the trimer is longer, as can be seen in Fig. 10. This graph shows the interaction energy calculated for the trimer in acetonitrile as a function of the interplanar separation between layers (the interplanar separation between the first and the second layer is the same as between the second and the third at each point of the curve). For comparison with the dimer, depicted in the same graph, the plotted energies were normalized to the number of π -pairs, in this case two. Interestingly, the binding between two cations doesn't seem to be impaired by the presence of a third one: the interaction between stacks remains almost constant, even though the equilibrium distance increases in about 0.1 Å. This suggests that the energetic and structural results found for the cation dimers will have applicability, to a large extent, to the case of more complex, larger aggregates consisting of multiple layers.

IV. SUMMARY

Our study has permitted to individualize the role of the surface tension and the dielectric screening in the stabilization of charged thiophene oligomer and polymer stacks. The surface tension of the solvent is a driving force toward the minimization of the cavity area, and therefore toward dimerization: there is an energetic payoff in accommodating two solutes in a single cavity of an area smaller than twice the one corresponding to the dissociated components. On the other hand, the dependence of the dimer stability on the polarity of the solvent alone is less evident. A dielectric effect is necessary to screen the electrostatic repulsion and to stabilize the charges in a small volume, but once the permittivity has

reached a certain threshold, a further increase in polarity has a negligible contribution to the stabilization of the system. This observation is probably general to any π -dimer of charged radicals—an hypothesis that could be interesting to test through explicit calculation.

The formation of trimers follows the same geometrical arrangement as the dimerization. A π -bond on one of the oligomer planes does not seem to significantly affect the bond on the other. These results point to the conclusion that the organization of aggregates and stacks is governed by the same thermodynamics that is already manifest in the dimerization.

V. ACKNOWLEDGMENTS

This research was supported by the MURI Grant DAAD 19-03-1-0169, by the Institute of Soldier Nanotechnologies, contract DAAD-19-02-D0002, and by Fundación Antorchas.

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under contract W-7405-Eng-48.

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- ¹ T.-Q. Nguyen, J. Wu, V. Doan, B. J. Schwartz, and S. H. Tolbert, *Science* **288**, 652 (2000).
- ² T.-Q. Nguyen, R. C. Kwong, M. E. Thompson, and B. J. Schwartz, *Appl. Phys. Lett.* **76**, 2454 (2000).
- ³ T.-Q. Nguyen, B. J. Schwartz, R. D. Schaller, J. C. Johnson, L. F. Lee, L. H. Haber, and R. J. Saykally, *J. Phys. Chem. B* **105**, 5153 (2001).
- ⁴ P. Kumar, A. Mehta, S. M. Mahurin, S. Dai, M. D. Dadmun, B. G. Sumpter, and M. D. Barnes, *Macromolecules* **37**, 6132 (2004).
- ⁵ A. D. W. Carswell, E. A. O'Rear, and B. P. Grady, *J. Am. Chem. Soc.* **125**, 14793 (2003).
- ⁶ H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig, and D. M. de Leeuw, *Nature* **401**, 685 (1999).
- ⁷ A. Ferretti, A. Ruini, E. Molinari, and M. J. Caldas, *Phys. Rev. Lett.* **90**, 86401 (2003).
- ⁸ J. L. Brédas, J. P. Calbert, D. A. Filho da Silva, and J. Cornil, *Proc. Natl. Acad. Sci. U.S.A.* **99**, 5804 (2002).
- ⁹ D. Beljonne, G. Pourtois, C. Silva, H. Hennebicq, L. M. Herz, R. H. Friend, G. D. Scholes, S. Setayesh, K. Müllen, and J. L. Brédas, *Proc. Natl. Acad. Sci. U.S.A.* **99**, 10982 (2002).
- ¹⁰ F. C. Spano, *J. Chem. Phys.* **122**, 234701 (2005).
- ¹¹ E. Mishina, T. Tamura, H. Sakaguchi, L. Kulyuk, and S. Nakabayashi, *J. Chem. Phys.* **120**, 9763 (2004).
- ¹² E. W. H. Jager, E. Smela, and O. Inganäs, *Science* **290**, 1540 (2000).
- ¹³ M. Gross, D. C. Müller, H. Nothofer, U. Scherf, D. Neher, C. Bräuchle, and K. Meerholz, *Nature*

- 405**, 661 (2000).
- ¹⁴ T. M. Pappenfus, R. J. Chesterfield, C. D. Frisbie, K. R. Mann, J. Casado, J. D. Raff, and L. L. Miller, J. Am. Chem. Soc. **124**, 4184 (2002).
 - ¹⁵ D. A. Scherlis and N. Marzari, J. Am. Chem. Soc. **127**, 3207 (2005).
 - ¹⁶ M. G. Hill, J.-F. Penneau, B. Zinger, K. R. Mann, and L. L. Miller, Chem. Mater. **4**, 1106 (1992).
 - ¹⁷ L. L. Miller and K. R. Mann, Acc. Chem. Res. **29**, 417 (1996).
 - ¹⁸ E. Levillain and J. Roncali, J. Am. Chem. Soc. **121**, 8760 (1999).
 - ¹⁹ D. A. Scherlis and N. Marzari, J. Phys. Chem. B **108**, 17791 (2004).
 - ²⁰ S. Tsuzuki, K. Honda, and R. Azumi, J. Am. Chem. Soc. **124**, 12200 (2002).
 - ²¹ G. Brocks, J. Chem. Phys. **112**, 5353 (2000).
 - ²² D. A. Scherlis, J.-L. Fattebert, F. Gygi, M. Cococcioni, and N. Marzari, J. Chem. Phys. *in press?*
 - ²³ S. Baroni, A. Dal Corso, S. de Gironcoli, P. Giannozzi, C. Cavazzoni, G. Ballabio, S. Scandolo, G. Chiarotti, P. Focher, A. Pasquarello, K. Laasonen, A. Trave, R. Car, N. Marzari, A. Kokalj, <http://www.quantum-espresso.org/>.
 - ²⁴ D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
 - ²⁵ J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
 - ²⁶ J. Tomasi, B. Mennucci, and R. Cammi, Chem. Rev. **105**, 2999 (2005).
 - ²⁷ J.-L. Fattebert and F. Gygi, J. Comput. Chem. **23**, 662 (2002).
 - ²⁸ J.-L. Fattebert and F. Gygi, Int. J. Quantum Chem. **93**, 139 (2003).
 - ²⁹ M. Cococcioni, F. Mauri, G. Ceder, and N. Marzari, Phys. Rev. Lett. **94**, 145501 (2005).
 - ³⁰ D. D. Graf, R. G. Ruan, J. P. Campbell, L. L. Miller, and K. R. Mann, J. Am. Chem. Soc.

119, 5888 (1997).

- ³¹ J. Jakowski and J. Simons, *J. Am. Chem. Soc.* **125**, 16089 (2003).
- ³² P. Bäuerle, U. Segelbacher, A. Maier, and M. Mehring, *J. Am. Chem. Soc.* **115**, 10217 (1993).
- ³³ G. Zotti, G. Schiavon, A. Berlin, and G. Pagani, *Chem. Mater.* **5**, 430 (1993).
- ³⁴ P. Hapiot, P. Audebert, K. Monnier, J.-M. Pernaut, and P. Garcia, *Chem. Mater.* **6**, 1549 (1994).
- ³⁵ Standard density-functional theory would probably be a poor choice to explore this trend in long oxidized oligomers, given its inability to represent charge localization in a long, linear π -conjugated system, consequence of the self-interaction error. Alternative schemes as time-dependent density-functional theory or post-Hartree-Fock methods would be more suited to treat this problem.
- ³⁶ J. J. Apperloo and R. A. J. Janssen, *Synth. Met.* **101**, 373 (1999).

Figure Captions:

Figure 1.: A terthiophene dimer in the minimum energy configuration corresponding to the doubly-charged state, in which one singly-charged monomer is shifted 2.3 \AA with respect to the other along the main axis.

Figure 2.: Interaction energy as a function of the axial shift for the oxidized terthiophene and quaterthiophene dimers in acetonitrile.

Figure 3.: Interaction energy as a function of the axial shift for the oxidized terthiophene dimer in water ($\epsilon_0=78.8$, $\gamma=72.2 \text{ mN/m}$), acetonitrile ($\epsilon_0=35.7$, $\gamma=28.7 \text{ mN/m}$), and dichloromethane ($\epsilon_0=8.9$, $\gamma=27.2 \text{ mN/m}$).

Figure 4.: Interaction energy as a function of the interplanar separation between two singly-charged terthiophene cations in water, acetonitrile, and dichloromethane.

Figure 5.: Interaction energy as a function of the interplanar separation for the doubly-charged dimers of polyquaterthiophene (open symbols) and terthiophene (closed symbols) in dichloromethane and acetonitrile.

Figure 6.: (a) Interaction energy of two terthiophene cations in acetonitrile and in water, as a function of its separation. Open symbols curves were calculated omitting the cavitation contribution to the solvation energy, while the closed symbols curves include both the electrostatic and cavitation contributions. (b) Area of the solvation cavity as a function of the separation between the terthiophene cations. Beyond 4.75 \AA the cavity splits in two, and the plotted area corresponds to two cavities containing one singly-charged terthiophene each.

Figure 7.: Interaction energy between two terthiophene cations at a fixed separation as a function of the dielectric constant of the solvent, omitting the cavitation energy term, for

two different thresholds ρ_0 . The positive drift observed at high permittivity for $\rho_0=0.00078$ e is an artifact of the continuum model (see text).

Figure 8.: Minimum energy structures for the terthiophene trimer in acetonitrile, surrounded by its corresponding solvation cavities defined by isosurfaces at $0.00078e$.

Figure 9.: Interaction energy as a function of the axial shift between a doubly-charged terthiophene dimer and a third terthiophene cation in acetonitrile.

Figure 10.: Interaction energy as a function of the interplanar separation between three parallel terthiophene cations in acetonitrile. The top and the bottom layers are overlapping with each other, having an axial shift of 2.3 \AA with respect to the central layer, as shown in Fig. 8a.

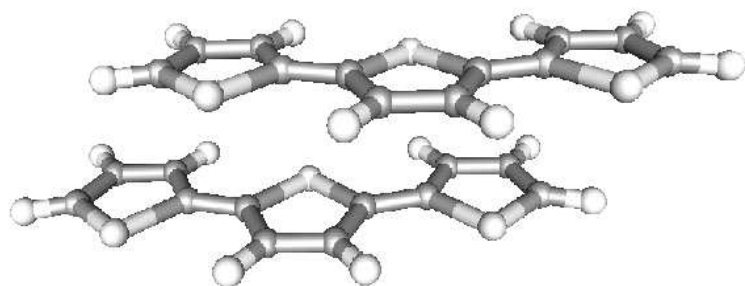


FIG. 1: D. Scherlis

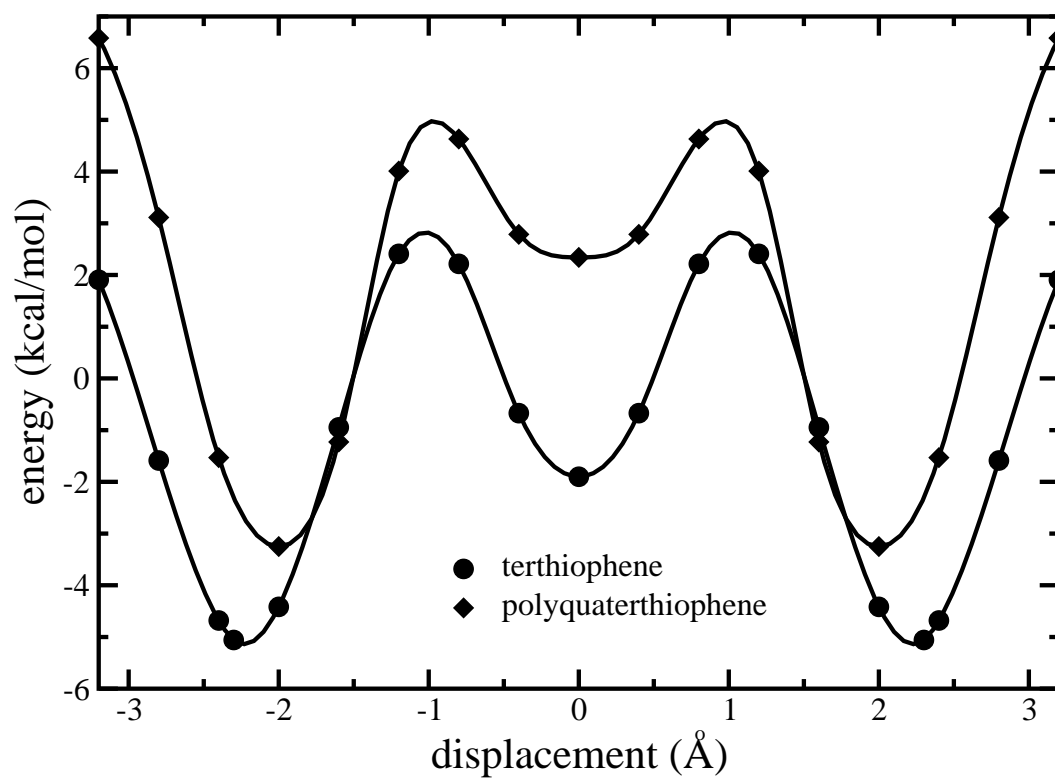


FIG. 2: D. Scherlis

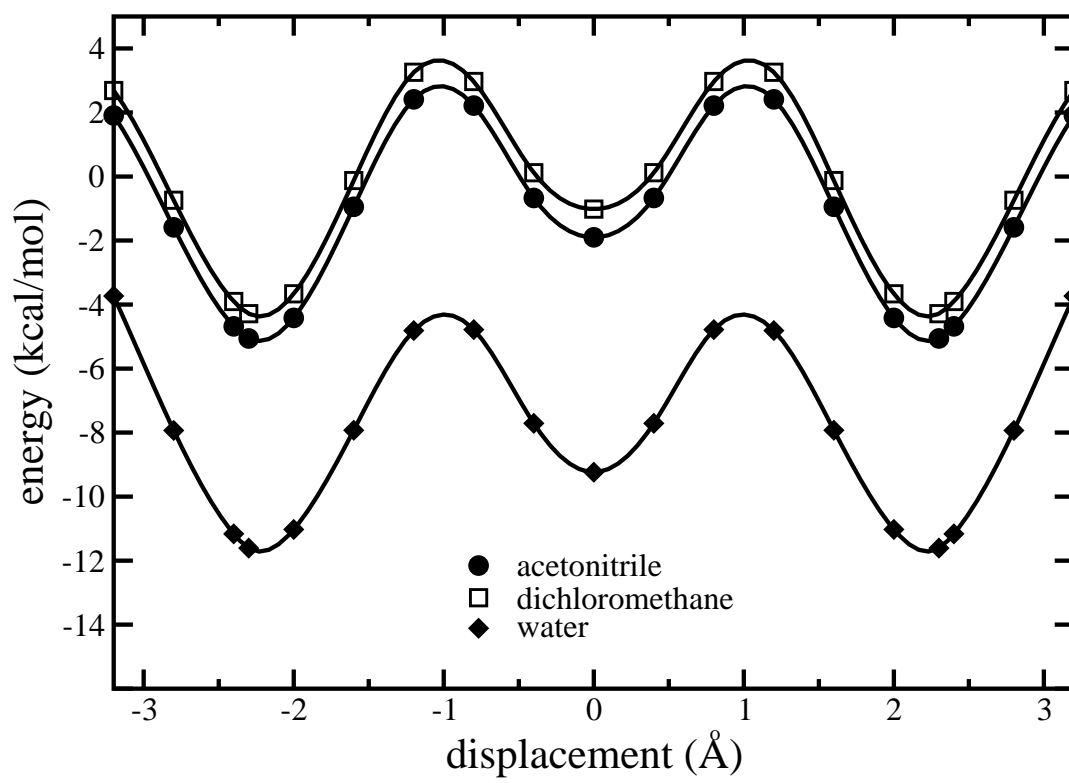


FIG. 3: D. Scherlis

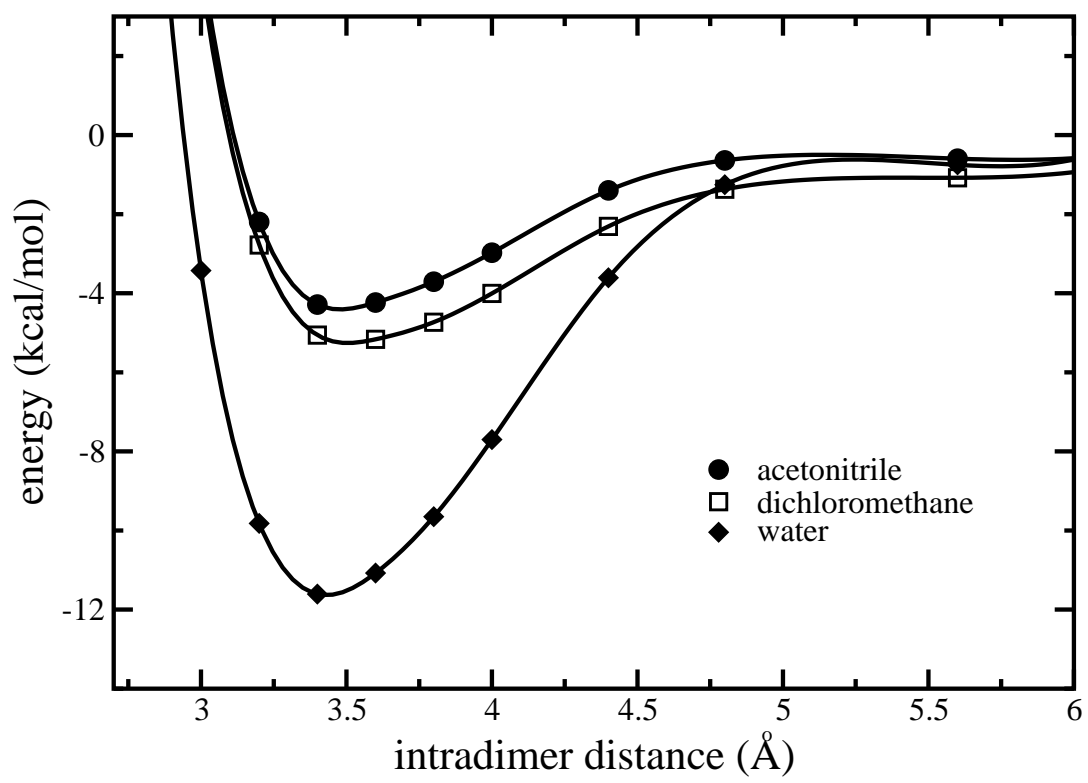


FIG. 4: D. Scherlis

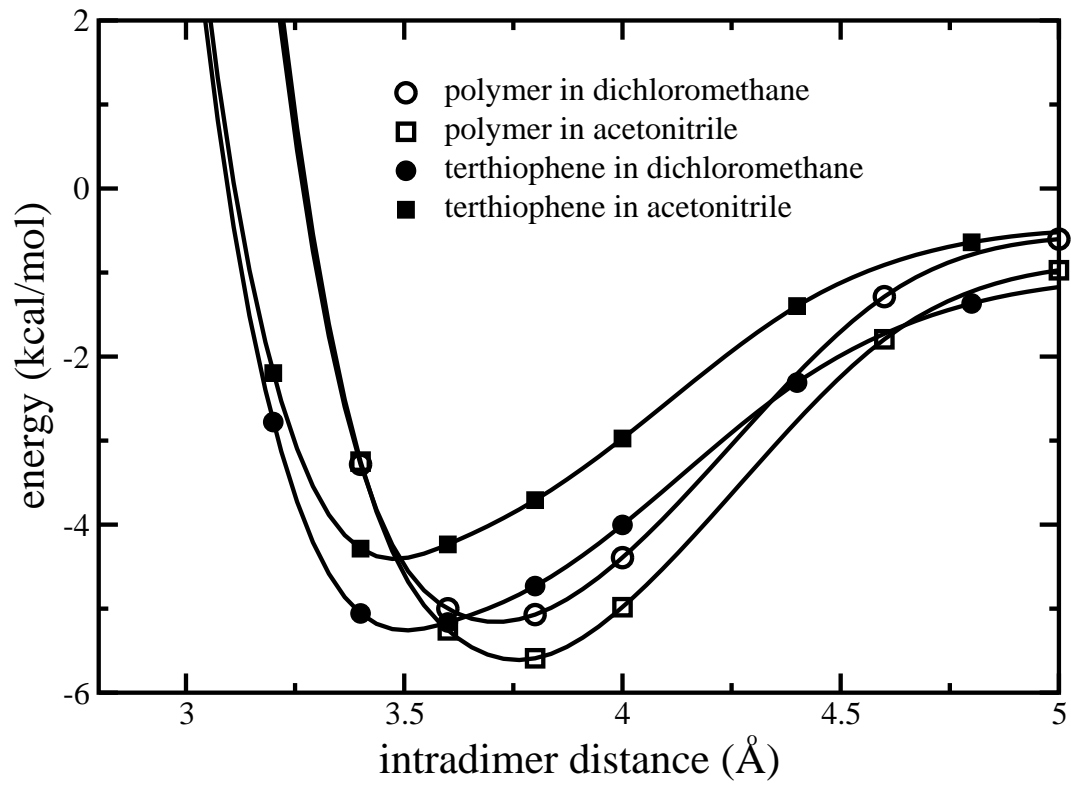


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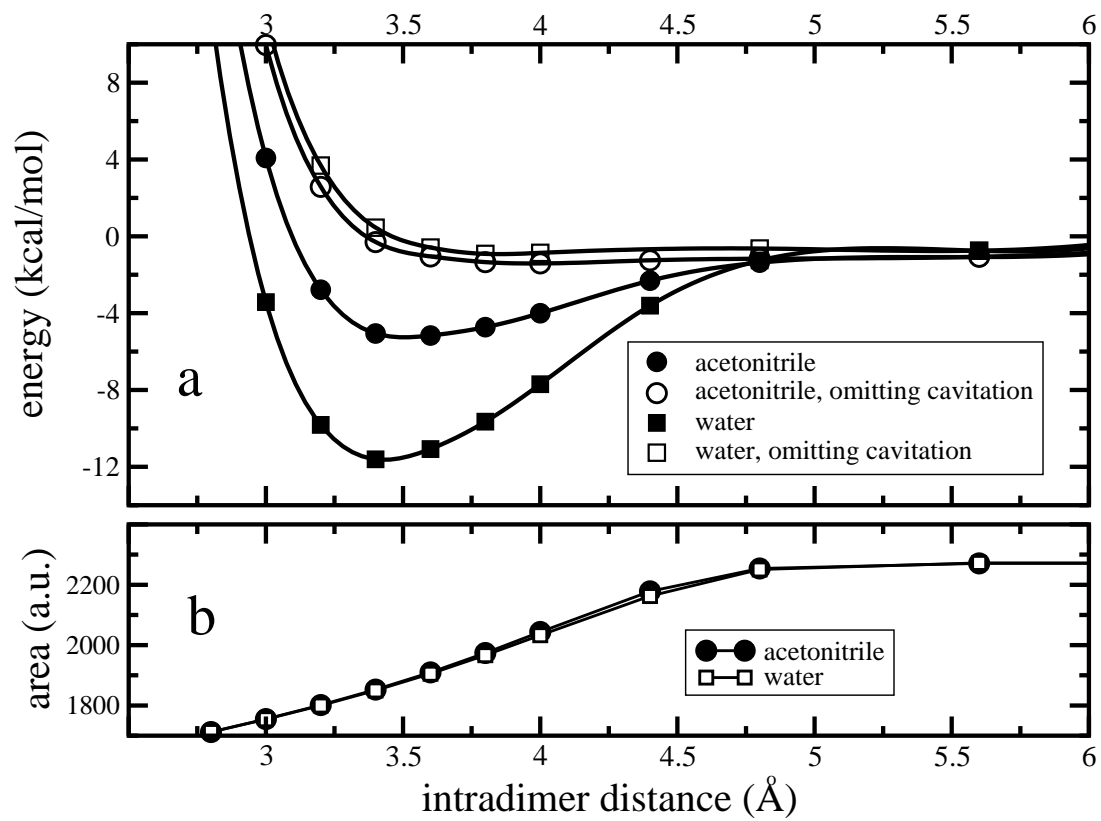


FIG. 6: D. Scherlis

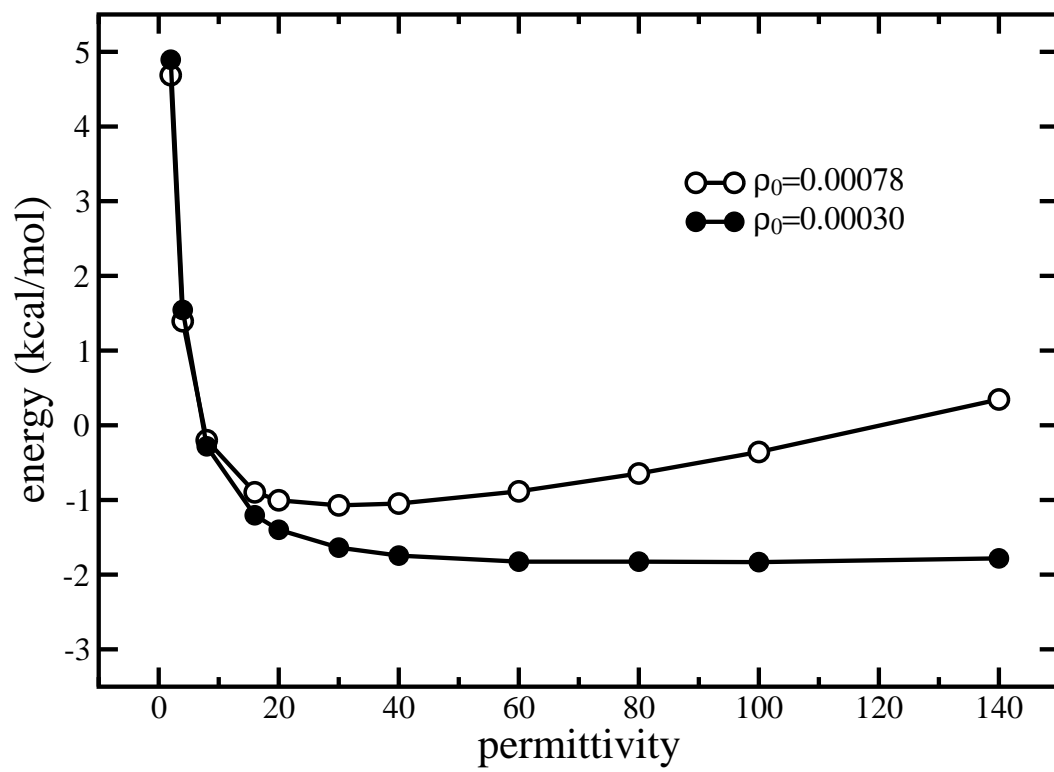


FIG. 7: D. Scherlis

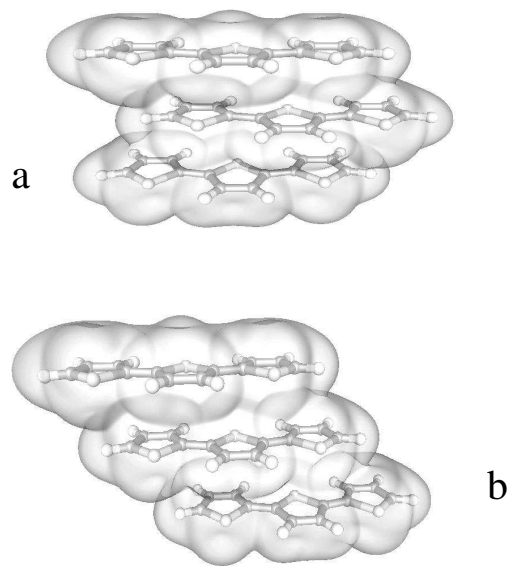


FIG. 8: D. Scherlis

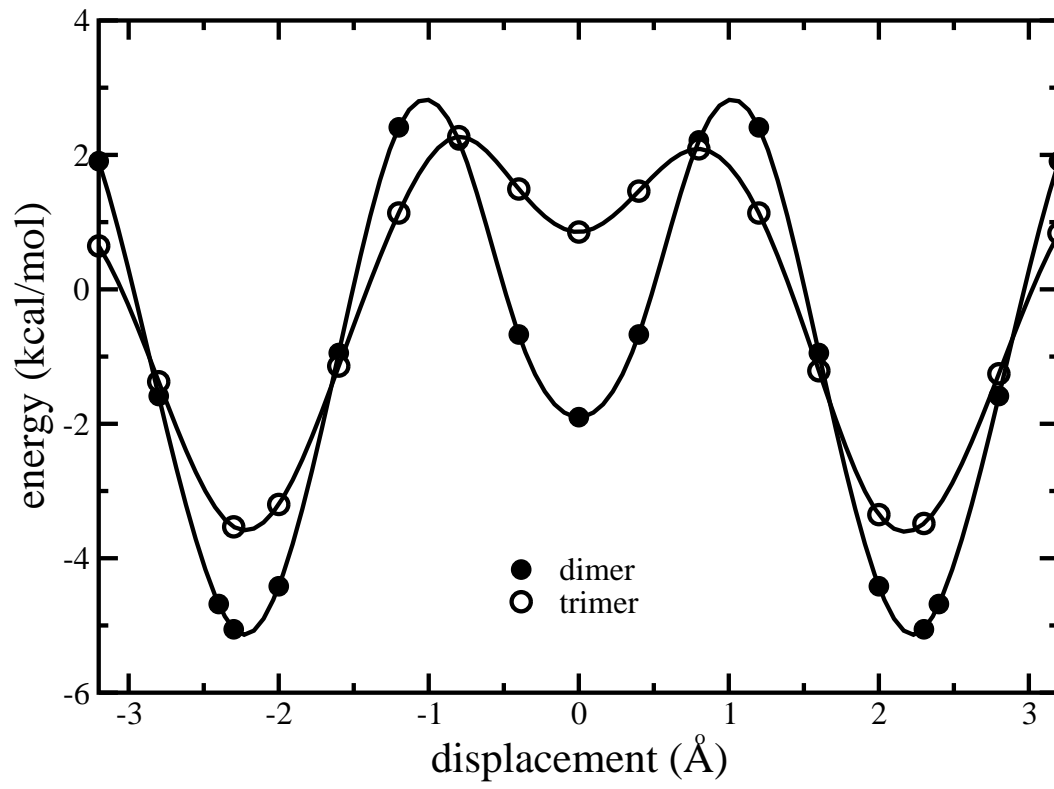


FIG. 9: D. Scherlis

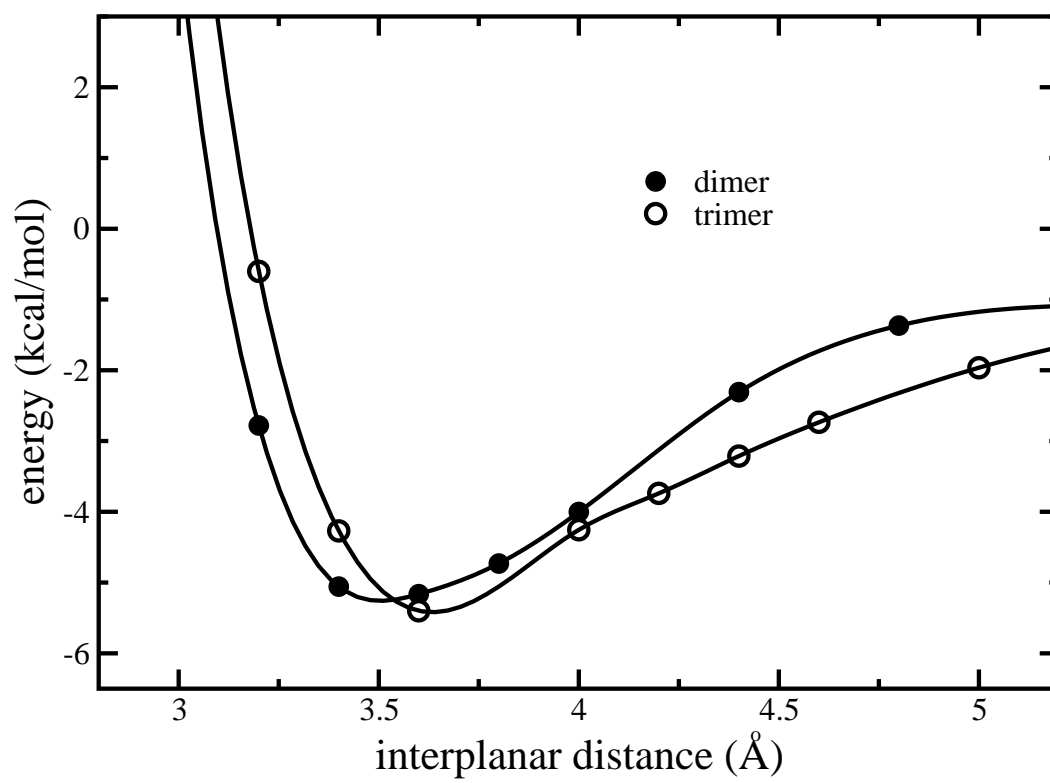


FIG. 10: D. Scherlis